CLAIMS

1. A method of producing polycrystalline silicon with high purity by a gas phase reaction between silicon tetra-chloride and zinc in a reaction furnace characterized by comprising the steps of:

placing silicon seed crystals in the reaction furnace keeping inner temperature at 910℃ or more in advance, and

depositing the silicon on the seed crystals.

2. The method of producing the silicon as claimed in claim 1 characterized in that a part of by-product zinc chloride in the reaction furnace is mixed with raw material gasses for use as circulating gas.

3. The method of producing the silicon as claimed in claim 1 characterized in that a gas-solid separation vessel is positioned at a top of the reaction furnace for separating the circulating gas and the produced silicon and the fine particle silicon going upward with the circulating gas is separated and returned to the reaction furnace.

4. The method of producing the silicon as claimed in claim 1 characterized in that by-product zinc chloride including non-reacted zinc and/or silicon tetra-chloride is taken out through a by-pass and eliminated from a reaction system with cooling and

liquefying such that system pressure is maintained at 5 atm. or less.

5. The method of producing the silicon as claimed in claim 1 characterized in that the zinc chloride separated by liquefaction from a reaction system is used as electrolyte to be decomposed to chlorine and the zinc by molten salt electrolysis, the zinc is used for reducing silicon tetra-chloride and the chlorine is reacted with the raw material metal silicon to be converted into silicon tetra-chloride which is then reused and circulated.

6. The method of producing the silicon as claimed in claim 1, wherein the reaction furnace and/or an apparatus for taking out circulating gas and product having its inner surface coated with silicon by a CVD method in advance.

7. The method of producing the silicon as claimed in claim 1, wherein the reaction furnace is a fluidized bed system in which the seed crystals are flown by circulating gas in it.

8. The method of producing the silicon as claimed in claim 1, wherein the reaction furnace is a rotary kiln type having its heater outside.

9. The method of producing the silicon as claimed in claim 1, wherein the reaction furnace is a fixed bed system in which the seed crystals are not moved.

10. A method of producing silicon characterized by comprising the steps of:

conducting a gas phase reaction between silicon tetra-chloride and zinc in a reaction melting furnace keeping its inner wall temperature from 1410℃ to 1600℃, and

condensing silicon melt produced in the reaction melting furnace for obtaining molten silicon.

11. The method of producing the silicon as claimed in claim 10 characterized in that the reaction melting furnace is a cyclone melting furnace where reaction gases and atmospheric gas are circulated with spiral flow in the reaction furnace.

12. The method of producing the silicon as claimed in claim 10 characterized in that a re-melting furnace in which non-melted fine crystal silicon and/or non-condensed silicon melt in the reaction melting furnace is collected and melted is positioned adjacent to a lower part of the reaction melting furnace.

13. The method of producing the silicon as claimed in claim 10 characterized in that a clearing furnace for clearing and de-gassing the molten silicon obtained in the reaction melting furnace and the re-melting furnace.

14. The method of producing the silicon as claimed in claim 10

characterized in that quartz glass is used for the reaction melting furnace, the re-melting furnace and the clearing furnace themselves or their inner surface lining for protecting from contamination of impurities from the furnace walls to the produced silicon during the reaction, the re-melting and the clearing.

15. The method of producing the silicon as claimed in claim 10 characterized in that magnesium oxide is used for the reaction melting furnace, the re-melting furnace and the clearing furnace themselves or their inner surface lining for protecting from contamination of impurities from the furnace walls to the produced silicon during the reaction, the re-melting and the clearing.

16. The method of producing the silicon as claimed in claim 10 characterized in that atmospheric gas in a reaction melting furnace, a re-melting furnace and a clearing furnace is zinc chloride or mixed gas of zinc chloride and argon.

17. The method of producing the silicon as claimed in claim 10 characterized in that inside of a clearing furnace is pressure-reduced by cooling and liquefied-removing produced zinc chloride and the non-reacted zinc or the silicon tetra-chloride by using a cooling apparatus attached to a clearing furnace for facilitating release of gas trapped in the molten silicon.

18. The method of producing the silicon as claimed in claim 10

characterized in that the molten silicon in the clearing furnace is taken out into a vessel such as a crucible and is gradually cooled for obtain polycrystalline or monocrystal silicon.

19. The method of producing the silicon as claimed in claim 10 characterized in that zinc chloride separated from a reaction system by liquefaction is used as electrolyte to be decomposed into chlorine and zinc through molten salt electrolysis, and the zinc is re-used for reduction of silicon tetra-chloride, and the chlorine is re-used to be reacted with raw material metal silicon for circulation.

20. A method of producing polycrystalline silicon by means of a gas-phase reaction between silicon tetra-chloride and zinc in a reaction furnace characterized by comprising the steps of:

conducting the gas phase reaction in the reaction furnace having inner temperature from 907℃ to 1410℃ to deposit silicon crystals,

increasing the inner temperature of the reaction furnace to 1410℃ or more to melt the silicon crystals,

moving the silicon melt, as molten liquid, into a vessel outside of the reaction furnace, and

solidifying or recrystallizing the molten liquid by cooling at 1410℃ or less in the vessel.

21. The method of producing the silicon as claimed in claim 20

characterized in that supply of reaction gas is stopped after the silicon crystals are deposited in the reaction furnace.

22. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that inside of the reaction furnace is pressure-reduced at atmospheric pressure or less for facilitating release of gas in silicon molten liquid when inside temperature of the reaction furnace is increased to 1410℃ to 1600℃ for melting the silicon.

23. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that the step of the reaction and the crystallization conducted at temperature from 907 to 1410℃ and the other step of increasing the inside temperature of the reaction furnace to 1410℃ to 1600℃ for melting the silicon which is taken out as the molten liquid are continuously and alternately conducted.

24. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that a part of by-product zinc chloride is used as atmospheric gas.

25. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that by-product zinc chloride including non-reacted zinc and/or silicon tetra-chloride is taken out through a by-pass and eliminated from a reaction system with

cooling and liquefying such that system pressure is maintained at 5 atm. or less.

26. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that zinc chloride separated from a reaction system by liquefaction is used as electrolyte to be decomposed into chlorine and zinc through molten salt electrolysis, and the zinc is re-used for reduction of silicon tetra-chloride, and the chlorine is re-used to be reacted with raw material metal silicon for circulation.

27. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that a furnace inner wall of the reaction furnace is made of quartz glass.

28. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that silicon seed crystals are placed in the reaction furnace in advance and the silicon is deposited on the seed crystals.

29. The method of producing the polycrystalline silicon as claimed in claim 20 characterized in that the reaction furnace having an inner wall coated with CVD silicon produced by the reaction is repeatedly used so that the silicon adhered on the inner wall of the reaction furnace is utilized as seed crystals.

30. A method of producing high purity silicon characterized by comprising the steps of:

producing the silicon by reacting silicon tetra-chloride gas with zinc gas in zinc chloride atmosphere, and

introducing the silicon to a silicon reservoir held at silicon-melted temperature or more for cooling and solidification.

31. The method of producing the polycrystalline silicon as claimed in claim 30 characterized in that dissolved gas is removed after the silicon is introduced to the silicon reservoir.

32. A method of producing high purity silicon characterized by comprising the steps of:

producing the silicon by reacting silicon tetra-chloride gas with zinc gas in zinc chloride atmosphere;

introducing the silicon to a silicon reservoir held at silicon-melted temperature or more;

removing dissolved gas; and

taking out the silicon as monocrystal silicon by using an apparatus for producing monocrystal silicon.

33. A method of producing high purity silicon characterized by comprising the steps of:

producing the silicon by reacting silicon tetra-chloride gas with zinc gas in zinc chloride atmosphere;

introducing the silicon to a silicon reservoir held at

silicon-melted temperature or more;

removing dissolved gas; and

sending to a cooling vessel to produce polycrystalline silicon by means of gradual cooling.

34. A method of producing high purity silicon characterized by comprising the steps of:

producing the silicon by reacting silicon tetra-chloride gas with zinc gas in zinc chloride atmosphere;

introducing the silicon to a silicon reservoir held at silicon-melted temperature or more;

removing dissolved gas; and

drastically scattering and semi-rapidly cooling the molten silicon for producing particulate silicon.

35. The method of producing the high purity silicon as claimed in claim 30 characterized in that the reaction between the zinc chloride and the silicon tetra-chloride gas is conducted from 1000℃ to 1500℃.

36. The method of producing the high purity silicon as claimed in claim 30 characterized in that the molten silicon reservoir has two compartments with a path at bottom, one of which is connected to a reaction section and the other is connected to reduced pressure atmosphere, and the silicon produced in the reaction section is accumulated in the reaction section of the molten silicon reservoir

and continuously moved to a pressure-reduced section of the reservoir for de-gasification.

37. The method of producing the high purity silicon as claimed in claim 30 characterized in that the argon gas is supplied through a bottom of the molten silicon reservoir for conducting de-gasification and agitation.

38. The method of producing the high purity silicon as claimed in claim 30 characterized in that a part of the zinc chloride in a reaction section is sent to an electrolytic cell after liquefaction by cooling for separating chlorine from zinc by means of electrolysis for re-use.

39. The method of producing the high purity silicon as claimed in claim 30 characterized in that reaction gas temperature is higher than that of the furnace wall and the inner wall surface of a reaction section is substantially coated with solid silicon such that no reaction takes place between the produced silicon and the inner wall.

40. The method of producing the high purity silicon as claimed in claim 30 characterized in that temperature of the silicon reservoir is controlled by induction heating to hold the inner wall temperature of the reservoir lower than a melting point of the silicon, and the silicon itself is held in a molten state.

41. A method of producing high purity using silicon tetra-chloride as raw material comprising the steps of:

1) performing a gas phase reaction between silicon tetra-chloride and metal zinc in zinc chloride gas in a reaction furnace;

2) separating produced metal silicon in a liquid state from gas;

3) separating a part of the zinc chloride gas which is cooled and liquefied;

4) electrolyzing the liquid zinc chloride to produce chlorine gas and molten zinc;

5) vaporizing the produced molten zinc by heating which is sent to the reaction furnace;

6) reacting the chlorine gas produced by the electrolysis with coarse silicon to generate coarse silicon tetra-chloride;

7) purifying the coarse silicon tetra-chloride by means of distillation; and

8) vaporizing the purified silicon tetra-chloride which is sent to the reaction furnace.

42. The method of producing the high purity silicon as claimed in claim 41 characterized by further comprising a step of eliminating the reaction gas contained in the metal silicon between the steps 2) and 3).

43. The method of producing the high purity silicon as claimed in claim 41 characterized in that the reaction furnace is a cyclone melting furnace in which reaction gasses are circulated by atmospheric gas circulating therein for performing the reaction, thereby minimizing contact with a side wall of the reaction furnace.

44. The method of producing the high purity silicon as claimed in claim 41 characterized in that reaction temperature is 1300℃ or more, and the silicon produced in the reaction goes downward as fine particle and/or liquid drop to be held in a silicon melt reservoir placed below the reaction furnace.

45. The method of producing the high purity silicon as claimed in claim 41 characterized in that the gas component in the produced silicon melt is eliminated by passing argon gas through the silicon melt.

46. The method of producing the high purity silicon as claimed in claim 41 characterized in that the electrolysis of the zinc chloride is conducted without support electrolyte.

47. The method of producing the high purity silicon as claimed in claim 41 characterized in that the chlorine gas generated by the electrolysis of the zinc chloride is taken out from an upper part of the electrolytic cell and the molten zinc from a bottom part.

48. The method of producing the high purity silicon as claimed in claim 41 characterized in that the chlorine gas generated by the electrolysis is in contact with raw material metal silicon at the higher temperature to be converted into coarse silicon tetra-chloride which is liquefied and stored at ordinary temperature and then purified with distillation for use as raw material silicon tetra-chloride so that the generated chlorine is not required to be stored as gas or liquid.

49. An apparatus for producing silicon for obtaining solid or liquid silicon and gaseous zinc chloride through a gas-phase reaction between silicon tetra-chloride and zinc comprising:

a reaction furnace section;

a silicon reservoir section placed below the reaction furnace section;

an inlet of reaction gas;

an outlet of produced zinc chloride gas; and

a refractory and electrically conductive trap equipped with a heating mechanism for collecting the solid or liquid silicon produced by the reaction in the reaction furnace,

wherein the trap is heated to silicon melting temperature or more during or after cease of supply of the reaction gas for liquefying the silicon which is then sent to the silicon reservoir section.

50. The apparatus for producing the silicon as claimed in claim 49 characterized in that the silicon reservoir section is placed below the reaction furnace section, and the silicon melted in the reaction furnace is sent to the reservoir section by gravity.

51. The apparatus for producing the silicon as claimed in claim 49 characterized in that temperature of heating the reaction furnace section is from 910℃ to 1500℃, and a temperature control mechanism which can arbitrary maintain the temperature in the temperature region is provided.

52. The apparatus for producing the silicon as claimed in claim 49 characterized in that an inner wall of the reaction furnace is mainly made of quartz glass.

53. The apparatus for producing the silicon as claimed in claim 49 characterized in that an inner wall of the reaction furnace is made of tantalum which is concurrently heated with the trap.

54. The apparatus for producing the silicon as claimed in claim 49 characterized in that the reaction furnace is a cyclone furnace, and the trap is a mesh positioned inside of the reaction furnace inner wall.

55. The apparatus for producing the silicon as claimed in claim 49 characterized in that porous and/or mesh type metal is

filled in the reaction furnace.

56. The apparatus for producing the silicon as claimed in claim 49 characterized in that the trap is a porous and sintered member for a metal filter placed in the reaction furnace.

57. The apparatus for producing the silicon as claimed in claim 49 characterized in that the refractory and electrically conductive trap is made of tantalum and/or molybdenum.

58. The apparatus for producing the silicon as claimed in claim 49 characterized in that the refractory and electrically conductive trap is heated by induction heating.

59. The apparatus for producing the silicon as claimed in claim 49 characterized in that the refractory and electrically conductive trap is heated by direct electric power current to the trap.

60. A method of producing silicon for obtaining solid or liquid silicon and gaseous zinc chloride through a gas-phase reaction between silicon tetra-chloride and zinc comprising the steps of:

placing a refractory and electrically conductive trap for collecting the solid or liquid silicon produced by the reaction in the reaction furnace; and

heating the trap to silicon melting temperature or more

during or after cease of supply of the reaction gas for liquefying the produced silicon for collection.

61. The method of producing the silicon as claimed in claim 60 characterized in that the reaction is performed from 910℃ to 1500℃.

62. The method of producing the silicon as claimed in claim 60 characterized in that atmospheric gas is zinc chloride.

63. The method of producing the silicon as claimed in claim 60 characterized in that a stoichiometric excess amount of zinc gas is supplied with respect to silicon tetra-chloride.

64. The method of producing the silicon as claimed in claim 60 characterized in that the heating temperature of the trap is from 1410℃ to 1500℃.

65. The method of producing the silicon as claimed in claim 60 characterized in that the silicon produced in a reservoir section is maintained at 1410℃ or less.

66. The method of producing the silicon as claimed in claim 60 characterized in that the reserved silicon in the reservoir section is externally taken out after the silicon is melted and de-gasified.

67. The method of producing the silicon as claimed in claim 60 characterized in that the zinc chloride produced in the reaction is taken out from the system and is decomposed into chlorine and zinc through electrolysis, and the chlorine is used for silicon tetra-chloride production, and the zinc is returned to the reaction furnace section as reaction gas for re-circulation.

68. The method of producing the silicon as claimed in claim 60 characterized in that the supply gas is supplied to the reaction furnace after preheating.

69. A method of producing high purity silicon through a gas-phase reaction between silicon tetra-chloride and zinc in a reaction furnace comprising the steps of:

making the silicon not in contact with air during the reaction while reaction temperature is maintained at melting point of the silicon or less, and

obtaining the produced silicon as block or molten state.